INSA INSTITUT NATIONAL DES SCIENCES APPLIQUÉES LYON

FC – AMERINSA – ASINSA - EURINSA – SCAN –SHN
Monday 20 NOVEMBER 2023

Assessment of Chemistry 2 (2 hours)

- *No documents allowed. Any type of calculator allowed.*
- *Your answers and your approach must be justified. Literal formulas must clearly appear, then put into numerical form before giving the result of your calculations.*
- $R = 8.314\,\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ and $0\,°\mathrm{C} = 273\,\mathrm{K}$.

Exercise 1: (approximately 14 points)

Chloroform is an organochlorine compound with molecular formula $CHCl_3$. It is used in different applications such as, for example, solvent for several organic compounds or precursor in the formation of fluorinated polymers. Chloroform can be produced from methanol (CH_3OH), a process leading to the formation of a methanol-chloroform binary mixture that must be treated successively to separate the two components.

1st part : Pure components

The Clapeyron equation $\frac{dP}{dT} = \frac{\Delta_{vap}H°}{T\,\Delta V}$ can be integrated in the form: $\ln P^* = \frac{-\alpha}{T} + \beta$.

Methanol (A)

1. **Calculate**, in °C, the boiling temperature of methanol under 760 mmHg.
2. **Calculate**, in $\mathrm{kJ \cdot mol^{-1}}$, $\Delta_{vap}H°$ of methanol.

Chloroform (B)

3. **Calculate** the numerical values of α and β for the chloroform vaporisation. The accuracy on α will be within 1 and on β within 0.01.

2nd part: Methanol-chloroform binary mixture, hypothesis of ideal solution.

In this 2nd part, the methanol – chloroform mixture, investigated under a total pressure P of 760 mmHg, is supposed to form an ideal solution.

4. **Establish,** at the liquid/vapour equilibrium of the methanol – chloroform mixture, the literal expression of the chloroform molar fraction in the liquid phase (noted x_B) and of the chloroform molar fraction in the vapour phase (noted y_B) as function of the total pressure *P* and of the saturating vapour pressures P_A^* and P_B^*.
5. **Calculate** the composition in molar fraction of chloroform of the liquid and vapour phases at equilibrium at 63.0 °C under the total pressure *P* of 760 mmHg.

3rd part: Methanol-chloroform binary mixture, case of real solution.

From now on we will work on the methanol – chloroform mixture under the pressure of 760 mmHg using the experimental data shown in Table 2.

6. **Carefully draw the isobaric diagram** (on the graph millimetre paper provided in the appendix) of the methanol – chloroform mixture as function of the chloroform composition expressed as molar fraction and **mention all relevant information**.
7. What kind of miscibility does the methanol – chloroform mixture show?
8. What can you say about the interactions between methanol and chloroform?
9. What is the unique particularity of the mixture with a chloroform molar fraction equal to 0.651?

A kilogram of a methanol – chloroform mixture, noted M, of global mass composition in chloroform $w_{M,B} = 0.651$ is brought to the temperature of 57.1 °C under 760 mmHg.

10. What are, at this temperature, the molar composition and the mass of the present phase (or phases)?

A ton of the same mixture M, $w_{M,B} = 0.651$, is introduced in a facility of fractioned distillation.

11. If the fractionation facility is sufficiently efficient: what (nature, composition, mass) will the residue and the distillate of the distillation will be made of?

Data

Component A (methanol):

$M_A = 32\ \mathrm{g \cdot mol^{-1}}$

$\ln P^*_{A\,(\mathrm{mmHg})} = \frac{-4498}{T} + 19.96$

Component B (chloroform):

$M_B = 119.4\ \mathrm{g \cdot mol^{-1}}$

Table 1 : Saturating vapour pressures of chloroform as function of the temperature.

θ (°C)	**50.5**	**74.0**
P^*(mmHg)	529	1133

Mixture A – B:

Table 2 : Chloroform molar composition of the liquid (x_B) and vapour (y_B) phase at equilibrium of a methanol-chloroform mixture at several temperatures and under a total pressure of 760 mmHg.

θ (°C)	**63.0**	**60.0**	**57.1**	**54.6**	**53.9**	**54.5**	**56.0**	**58.0**	**59.8**	**61.3**
y_B	0.100	0.262	0.417	0.558	0.651	0.726	0.791	0.872	0.941	1.000
x_B	0.037	0.115	0.234	0.424	0.651	0.844	0.925	0.969	0.988	1.000

Exercise 2: (approximately 6 points)

The 2 parts are independent.

Sulfuryl chloride is obtained by the following reaction:

$$SO_{2_{gas}} + Cl_{2_{gas}} \rightleftarrows SO_2Cl_{2_{gas}}$$

The equilibrium constants of this reaction at $353\ \mathrm{K}$ and $543\ \mathrm{K}$ are $\boldsymbol{K°_{353} = 1.64}$ and $\boldsymbol{K°_{543} = 1.6 \times 10^{-3}}$ respectively.

Part 1:

At $353\ \mathrm{K}$, we introduce in a reactor kept at a pressure of $3\ \mathrm{bar}$,

- 0.1 moles of Cl_2
- 0.4 moles of SO_2
- 0.15 moles of SO_2Cl_2

1. After calculating the $\Delta_r G$, give the direction of evolution of the system.

Part 2:

2. **Express** and **calculate** $\boldsymbol{\Delta_r G°}$, at $353\ \mathrm{K}$ and $543\ \mathrm{K}$.
3. **Calculate** the $\boldsymbol{\Delta_r H°}$ and the $\boldsymbol{\Delta_r S°}$ of the synthesis reaction, knowing that they are both temperature independent.
4. Comment on the sign of these quantities. In the case you cannot calculate them, what should the sign of these quantities be according to the elements you have?

Appendix: graph paper for the isobaric diagram (exercise 1).

End of the statement.